Iridium(III) Hydrido Complexes with 2-Pyridinaldazines. Crystal Structure of $[IrH_2(mpaa)(PPh_3)_2]SbF_6$.* Synthesis and Characterization of Homo- and Hetero-nuclear Complexes

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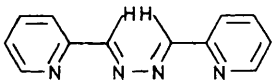
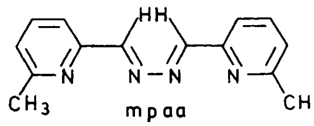
The reactivity of the hydrido complexes $[IrH_2(Me_2CO)_2(PPh_3)_2]X$ [X = PF_6, (**1a**) or SbF_6, (**1b**)] with 2-pyridinaldazines [2-pyridinecarbaldehyde azine (paa) and 6-methyl-2-pyridinecarbaldehyde azine (mpaa)] is reported. The molecular structure of both mononuclear complexes which form from (**1b**), $[IrH_2(N–N)(PPh_3)_2]SbF_6$ [N–N = paa, (**2b**); or mpaa (**3b**)], comprises an octahedral iridium(III) centre with apical PPh_3 and *cis* hydrido ligands, as shown by an *X*-ray analysis of (**3b**). The mononuclear species react further with the homologous parent compound (**1a**) or (**1b**) to afford the homobinuclear species $[\{IrH_2(PPh_3)_2\}_2(\mu\text{-N–N})]X_2$ (X = PF_6 or SbF_6). Moreover, the reaction of (**2a**) with $CuCl_2\cdot2H_2O$, $[PdCl_2(PhCN)_2]$ or $[PtMe_2(dmso)_2]$ leads to heterobimetallic complexes. The iridium(III)—platinum(II) compound undergoes oxidative addition with MeI, giving rise to the iridium(III)—platinum(IV) species $[(Ph_3P)_2H_2Ir(paa)PtMe_3I]PF_6$. All the new complexes have been characterized by elemental analysis, conductivity measurements, i.r., and ^1H and $^{31}P-\{^1H\}$ n.m.r. spectroscopy. Crystals of (**3b**) are triclinic, space group $P\bar{1}$, with a = 14.017(6), b = 15.673(7), c = 12.452(6) Å, α = 99.60(1), β = 112.78(2), γ = 97.88(2)°, and Z = 2. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares to R = 0.049 for 5 675 observed reflections.

The introduction of heterobimetallic complexes in catalytic processes takes advantage of the co-operative action of the two different metal centres.[1] Among the many aspects related to the understanding of this chemistry, within the present investigation we have considered the role played in the reactivity of iridium dihydrido species by a second transition metal, electronically communicating through a bis-chelating nitrogen-containing ligand but, chemically and sterically, discouraged with respect to M–M bond formation.

The synthesis of mononuclear six-co-ordinated rhodium(III) and iridium(III) *cis*-dihydro compounds containing a N–N chelate ligand of the 2,2′-bipyridine (bipy) family has been recently reported.[2–5] Such species, of general formula $[MH_2(N–N)(PPh_3)_2]X$ (M = Rh, X = ClO_4 or PF_6; M = Ir, X = BF_4, PF_6, or SbF_6), are usually synthesized by treating the complexes $[MH_2(Me_2CO)_2(PPh_3)_2]X$[6] with the appropriate N–N ligand and exhibit an octahedral geometry with the two PPh_3 groups located in apical positions.[3–5] For complexes containing the bis-chelating 3,6-bis(2′-pyridyl)pyridazine (dppn) ligand, $[IrH_2(dppn)(PPh_3)_2]X$ (X = PF_6 or SbF_6) the only binuclear species we were able to synthesize were the homobinuclear tetrahydrido complexes $[\{IrH_2(PPh_3)_2\}_2\{\mu\text{-}C_4HN_2(C_5H_4N)_2\text{-}3,6\}]X$ (X = PF_6 or SbF_6).[4]

In a bimetallic bis-chelate species, dppn imposes a *cis* geometry, therefore its inertness toward the formation of such compounds may be attributed to the steric crowding which would be caused by the ligands lying on the dppn plane. Thus, in this paper we report the reactivity of $[IrH_2(Me_2CO)_2(PPh_3)_2]X$ [X = PF_6 (**1a**) or SbF_6 (**1b**)] with 2-pyridinaldazines, a class of ligands containing two bipy-like chelating sites suitable for the formation of binuclear complexes.[7–10]


paa


mpaa

Results and Discussion

Mononuclear Complexes.—The cationic iridium(III) complex (**1a**) or (**1b**) readily reacts at 0 °C † with the ligands paa or mpaa (1 : 1 molar ratio in dichloromethane) leading to yellow or orange solutions from which air-stable microcrystalline compounds can be separated in good yields [equation (1)]. The products (**2**) and (**3**) in nitromethane solutions behave as 1 : 1 electrolytes[11] and show i.r., ^1H and $^{31}P-\{^1H\}$ n.m.r. spectra (see Experimental section and Table 1) in accord with *cis* terminal dihydrides.[4]

The synthesis of homologous rhodium dihydrides, from $[RhH_2(Me_2CO)_2(PPh_3)_2]PF_6$ under similar experimental con-

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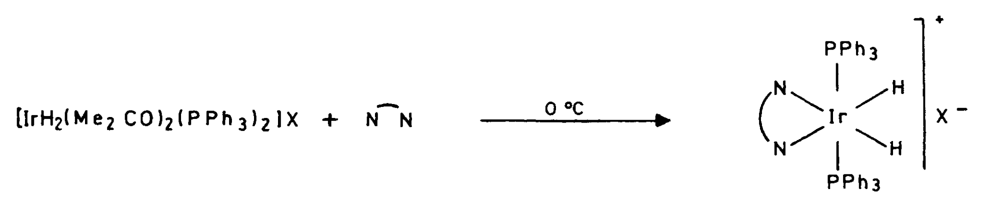
* Dihydrido(6-methyl-2-pyridinecarbaldehyde azine-*NN*$^{\alpha}$)bis(triphenylphosphine)iridium(III) hexafluoroantimonate(V).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

† Careful temperature control is required to prevent formation of tetrahydrido homobinuclear species.



	X
(1a)	PF_6
(1b)	SbF_6

	N N	X
(2a)	paa	PF_6
(2b)	paa	SbF_6
(3a)	mpaa	PF_6
(3b)	mpaa	SbF_6

Table 1. Proton[a] and $^{31}P\text{-}\{^1H\}$[b] n.m.r. data for the complexes

	Ir–H			
Complex	δ(H)	^2J(PH)/Hz	^2J(HH)/Hz	δ(P)
(2a)	−18.87	16.0	7.0	17.13
	−18.92	16.0	7.0	
(2b)	−18.86	17.0	6.7	17.38
	−18.91	16.6	6.7	
(3a)	−18.63	16.0	7.0	16.64
	−19.41	16.0	7.0	
(3b)	−18.63[c]	16.2	7.0	16.96
	−19.40	16.3	7.0	
(4a)	−18.61	17.0	6.3	14.12
	−21.47	20.2	6.3	
(4b)	−18.60	17.2	6.1	13.95
	−21.45	19.9	6.1	
(5a)	−19.57	18.4	6.2	12.39
	−20.83	19.8	6.2	
(5b)	−19.56	18.1	6.3	12.38
	−20.81	20.2	6.3	
(7)	−19.16	16.5	7.3	16.46
	−20.15	16.0	7.3	
(8)	−19.17	16.4	7.2	16.70
	−19.47	16.3	7.2	
(9)	−18.73	16.0	7.3	17.09[d]
	−19.26	16.0	7.3	19.89[d]

[a] In CD_2Cl_2 at 300 MHz and 25 °C; chemical shifts (δ) in p.p.m. to high frequency of internal $SiMe_4$. [b] In CD_2Cl_2 at 121.5 MHz and 25 °C, unless otherwise stated; chemical shifts (δ) in p.p.m. to high frequency of external 85% H_3PO_4. [c] Homonuclear decoupling experiments revealed a coupling with the N=CH proton [^4J(HH) = 1.0—1.3 Hz]. [d] In $(CD_3)_2CO$.

Table 2. Selected bond distances (Å) and angles (°) for complex **(3b)**

Ir–P(1)	2.314(4)	N(2)–C(6)	1.274(15)
Ir–P(2)	2.304(4)	N(2)–N(3)	1.441(11)
Ir–N(1)	2.165(10)	N(3)–C(7)	1.258(16)
Ir–N(2)	2.146(7)	C(7)–C(8)	1.47(2)
N(1)–C(1)	1.362(15)	C(8)–C(9)	1.35(2)
C(1)–C(2)	1.41(2)	C(9)–C(10)	1.39(2)
C(2)–C(3)	1.36(2)	C(10)–C(11)	1.37(2)
C(3)–C(4)	1.37(2)	C(11)–C(12)	1.37(2)
C(4)–C(5)	1.35(2)	N(4)–C(12)	1.351(16)
N(1)–C(5)	1.374(12)	N(4)–C(8)	1.352(15)
C(5)–C(6)	1.44(2)		
P(1)–Ir–N(1)	93.5(3)	N(1)–C(5)–C(6)	114(1)
P(1)–Ir–N(2)	94.6(3)	C(5)–C(6)–N(2)	120(1)
P(1)–Ir–P(2)	166.3(2)	Ir–N(2)–C(6)	116.0(7)
N(1)–Ir–N(2)	75.6(3)	Ir–N(2)–N(3)	133.1(7)
P(2)–Ir–N(1)	97.4(3)	N(3)–N(2)–C(6)	110.8(8)
P(2)–Ir–N(2)	96.1(2)	N(2)–N(3)–C(7)	114.4(8)
Ir–N(1)–C(1)	128.3(8)	N(3)–C(7)–C(8)	120(1)
Ir–N(1)–C(5)	114.3(7)	C(7)–C(8)–N(4)	113(1)
C(1)–N(1)–C(5)	117.4(10)	C(7)–C(8)–C(9)	122(1)
N(1)–C(1)–C(2)	119(1)	N(4)–C(8)–C(9)	125(1)
C(1)–C(2)–C(3)	121(1)	C(8)–C(9)–C(10)	117(1)
C(2)–C(3)–C(4)	119(2)	C(9)–C(10)–C(11)	120(1)
C(3)–C(4)–C(5)	119(1)	C(10)–C(11)–C(12)	119(1)
C(4)–C(5)–N(1)	124(1)	C(11)–C(12)–N(4)	123(1)
C(4)–C(5)–C(6)	122(1)	C(12)–N(4)–C(8)	116.1(10)

ditions, was unsuccessful because of the lability displayed by both the paa and mpaa ligands.

Crystal Structure of $[IrH_2(mpaa)(PPh_3)_2]SbF_6$ **(3b)**.—The crystal structure of complex **(3b)** consists of iridium cations and SbF_6^- anions. The structure of the cation is depicted in Figure 1 together with the atomic numbering system; selected bond distances and angles are given in Table 2. The octahedral co-ordination of the Ir atom involves two N atoms from mpaa acting as a chelating ligand through one pyridinic and one azinic N atom, two hydrides in *cis* positions, and two P atoms from PPh_3 ligands in *trans* positions. The hydrides have been located clearly in the Fourier difference map in the expected positions, even if at a slightly short distance from the metal [Ir–H′ 1.41, Ir-H″ 1.35 Å; H′–Ir–H″ 75°]. The Ir–N bond distances [2.165(10) and 2.146(7) Å], *trans* to the Ir-H ones, are comparable to those *trans* to H observed in the binuclear $[\{IrH_2(PPh_3)_2\}_2\{\mu\text{-}C_4HN_2(C_5H_4N)_2\text{-}3,6\}]^+$, 2.133(11) and 2.148(9) Å,[4] and in the mononuclear $[IrH(H_2O)(bquin)(PPh_3)_2]SbF_6$ (bquin = benzo[*h*]quinolinate), 2.10(2) Å.[12] These distances are much longer than those found in bipy complexes of Ir^{III} such as $[Ir(bipy)_3][ClO_4]_3$, average 2.04(1) Å,[13] and [Ir(bipy-*C*,*N*)(bipy-*N*,*N*′$)_2][ClO_4]_3$, average 2.053(5) Å,[14] for Ir–N *trans* to N, confirming the pronounced *trans* effect exerted by the H ligand.

The Ir–P bonds, 2.304(4) and 2.314(4) Å, are quite regular if compared with the corresponding bonds in binuclear and mononuclear iridium(III) complexes with bipy-like ligands in the equatorial plane.[4,12] As already observed for complexes of both Rh^{III} and Ir^{III},[3,4] the Ir–P bonds are slightly bent [P(1)–Ir–P(2) 166.3(2)°] towards the hydrides.

The conformation of the mpaa ligand is *trans,trans*, *i.e.* with the pyridyl groups on opposite sides of the N–N bond. The

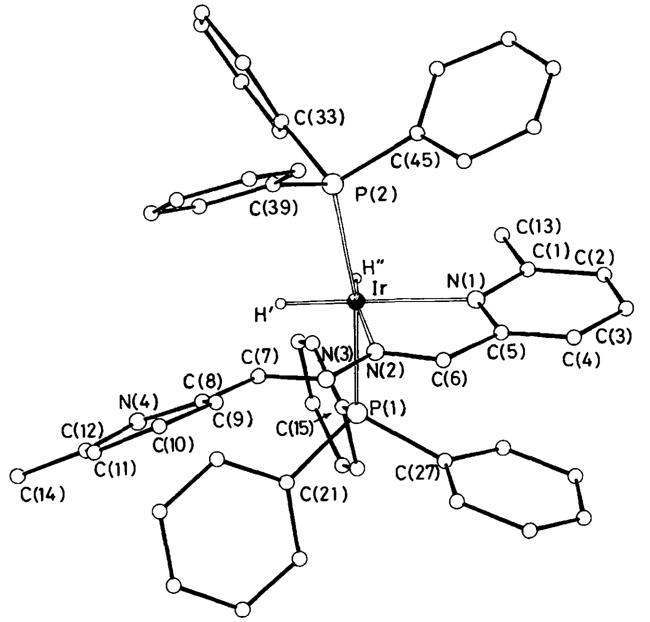


Figure 1. Perspective view of the structure of the cationic complex $[\mathrm{IrH_2(mpaa)(PPh_3)_2}]^+$ with the atomic numbering scheme

pyridyl not involved in co-ordination is tilted by about 29° with respect to the remaining moiety of the ligand which is planar.

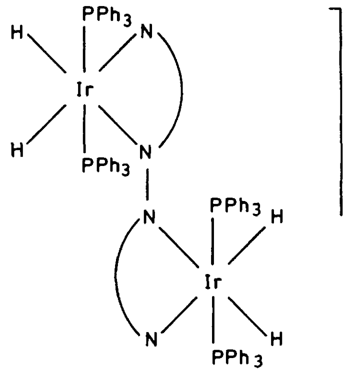
The dimensions of the $\mathrm{SbF_6}^-$ anions are quite regular with Sb–F bonds in the range 1.76(2)—1.86(2) Å, and the F–Sb–F angles, involving *cis*-F atoms, in the range 84.9(6)—96.2(8)°.

Bimetallic Homonuclear Complexes.—Treatment of mononuclear complexes (**2**) or (**3**) with (**1**) in dichloromethane at room temperature (r.t.) (1:1 molar ratio) gives red or dark red solutions, from which the expected binuclear products were recovered in good yields [equation (2)]. On the basis of elemental analysis and conductivity measurements (see Experimental section) the compounds (**4**) and (**5**) are formulated as the bridged species $[\{\mathrm{IrH_2(PPh_3)_2}\}_2(\mu\text{-N-N})]X_2$.

$$[\mathrm{IrH_2(N\frown N)(PPh_3)_2}]X + [\mathrm{IrH_2(Me_2CO)_2(PPh_3)_2}]X \xrightarrow{\text{r.t.}} [\{\mathrm{IrH_2(PPh_3)_2}\}_2(\mu\text{-}\mathrm{N\frown N})]X_2 \qquad (2)$$

			$\mathrm{N\frown N}$	X
(**2a**)	(**1a**)	(**4a**)	paa	$\mathrm{PF_6}$
(**2b**)	(**1b**)	(**4b**)	paa	$\mathrm{SbF_6}$
(**3a**)	(**1a**)	(**5a**)	mpaa	$\mathrm{PF_6}$
(**3b**)	(**1b**)	(**5b**)	mpaa	$\mathrm{SbF_6}$

All the new binuclear complexes display the same structural features. Thus the $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ n.m.r. spectra show a single resonance in the range δ 12—14 p.p.m., indicating equivalence of the four phosphines, while both the ^{1}H n.m.r. (Table 1) and i.r. data (Experimental section) are consistent with a *cis* $\mathrm{IrH_2}$ moiety. Moreover, in the ^{1}H n.m.r. spectra of either the paa or mpaa complexes a multiplicity in agreement with a symmetrical bis-chelating bonding mode is observed. Therefore, on this evidence, for the cations of (**4**) and (**5**) we suggest a structure containing two equivalent $\mathrm{IrH_2(PPh_3)_2}$ fragments, each co-ordinated to the binucleating ligands as in the previously discussed mononuclear species, probably arranged in an overall transoid geometry to remove the steric hindrance due either to the equatorial hydrido groups or to the bulky $\mathrm{PPh_3}$ which occupy the four apical positions.



Bimetallic Heteronuclear Complexes.—The synthesis of heterobimetallic complexes was carried out only starting from the mononuclear complex (**2a**). Mixed species of general formula $[\mathrm{(Ph_3P)_2H_2Ir(paa)ML_2}]\mathrm{PF_6}$ have been synthesized at room temperature from a dichloromethane solution of (**2a**) with 1 equiv. of $\mathrm{CuCl_2{\cdot}2H_2O}$, $[\mathrm{PdCl_2(PhCN)_2}]$, or $[\mathrm{PtMe_2(dmso)_2}]$ (dmso = dimethyl sulphoxide) respectively. From the reaction mixtures, orange $[\mathrm{(Ph_3P)_2H_2Ir(paa)CuCl_2}]\mathrm{PF_6}$ (**6**), red $[\mathrm{(Ph_3P)_2H_2Ir(paa)PdCl_2}]\mathrm{PF_6}$ (**7**) or green $[\mathrm{(Ph_3P)_2H_2Ir(paa)PtMe_2}]\mathrm{PF_6}$ (**8**) were recovered in high yields (Experimental section). The i.r. spectra in the solid state (KBr) show weak absorptions in the range 2 260—2 180 cm^{-1} characteristic of terminal Ir–H bonds. Further absorptions in the M–Cl stretching region[15] are observed for (**6**) and (**7**). The ^{1}H n.m.r. data for complex (**7**) indicate non-equivalent hydrides lying in the paa plane as well as an asymmetrically co-ordinated paa ligand (Table 1 and Experimental section). In addition, the single resonance present in the $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ n.m.r. spectrum is consistent with two equivalent mutually *trans* $\mathrm{PPh_3}$ ligands.

The ^{1}H and $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ n.m.r. characterization of the platinum derivative (**8**), performed at room temperature, shows that two species, in the ratio of *ca.* 2:1, are actually present in solution. The signals of the main product, which in the proton spectrum are in accord with an asymmetrically bis-chelated paa, two $\mathrm{PPh_3}$ molecules, an $\mathrm{IrH_2}$, and a $\mathrm{PtMe_2}$ group, are attributed to $[\mathrm{(Ph_3P)_2H_2Ir(paa)PtMe_2}]\mathrm{PF_6}$. In particular, the two hydrido resonances are found shifted slightly upfield with respect to the parent (**2a**) (δ −19.17 and −19.47 *vs.* −18.87 and −18.92), while the $\mathrm{PtMe_2}$ moiety gives two equally intense signals at δ 0.76 and 1.23 with ^2J(PtH) 85 and 90 Hz. The corresponding $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ signal is found at δ 16.70 p.p.m. The other product is the mononuclear complex (**2a**), recognized by comparison with the spectra of a pure sample (proton spectrum in Figure 2). It is

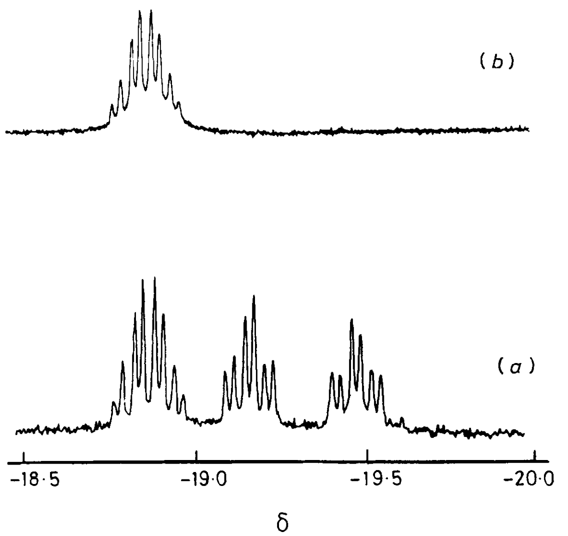
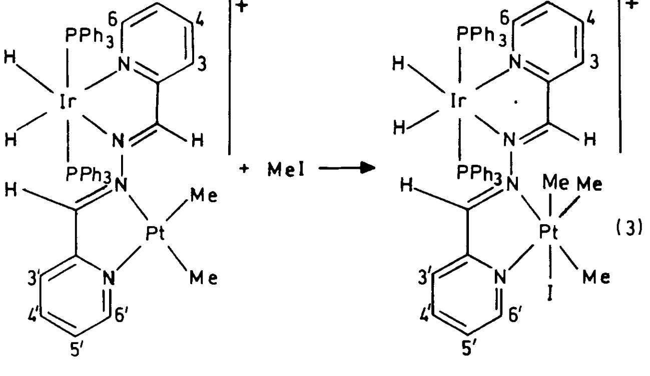


Figure 2. Proton n.m.r. spectra (300 MHz, CD_2Cl_2) of (*a*) $[(Ph_3P)_2H_2Ir(\mu\text{-paa})PtMe_2]PF_6$ (**8**) in the region of the hydride resonances and (*b*) $[IrH_2(paa)(PPh_3)_2]PF_6$ (**2a**)

noteworthy that the relative abundance of (**8**) and (**2a**) does not change significantly over several hours. Therefore we suggest that (**2a**) probably forms by a dissociative equilibrium of $PtMe_2$ from (**8**), although we were not able to determine the fate of the $PtMe_2$ fragment.

The heterobimetallic complex (**9**) has been prepared in acetone by the reaction of an excess of MeI with (**8**) (Experimental section). The product which immediately forms is the result of the oxidative-addition reaction of MeI to a platinum(II) centre [equation (3)] as in the reactions described in the literature for similar platinum derivatives.[16] Its ^1H n.m.r. spectrum is in accord with a single species, consequently this adduct is stable toward dissociation in solution. Furthermore, signals diagnostic of both a *cis*-IrH_2 (δ −18.73 and −19.26) and a $PtMe_3$ (δ 1.63, 1.36, and −0.32) moiety are observed. Regarding the platinum(IV) co-ordination sphere, these data are as expected for a MeI *trans* addition.[16] Moreover, the axial methyl group (δ −0.32) is strongly shielded,[16,17] probably due to the close iridium-bonded PPh_3 ligands. These two phosphines are magnetically non-equivalent, and give two distinct resonances at δ 17.09 and 19.89 p.p.m.



(**8**) (**9**)

Throughout the series of bimetallic heteronuclear compounds, the iridium exhibits an octahedral geometry as in (**3b**) (Figure 1). Moreover in complexes (**6**)—(**8**) the four-co-ordinate Cu^{II}, Pd^{II}, or Pt^{II} should be roughly square planar, while in (**9**) the six-co-ordinate Pt^{IV} is octahedral. So, regarding the structures, we suggest that they may be visualized as the result of a combination of two geometries, one for each metal, joined by the N–N bond of the paa.

Conclusions

The binucleating azine ligands paa and mpaa readily react with the iridium(III) *cis*-dihydrido complex $[IrH_2(Me_2CO)_2(PPh_3)_2]X$ (X = PF_6 or SbF_6) giving at room temperature binuclear derivatives. Thus the synthesis of the mononuclear species is achieved through careful control of the temperature.

The mononuclear species are very reactive toward the co-ordination of a second metal, and bimetallic heteronuclear complexes Ir^{III}–Cu^{II}, Ir^{III}–Pd^{II}, Ir^{III}–Pt^{II}, and Ir^{III}–Pt^{IV}, in addition to the homonuclear Ir^{III}–Ir^{III}, have been prepared.

As far as the hydrido iridium(III) compounds are concerned, it is known that with decreasing σ-donor strength of the *trans* ligand a high-field shift of δ(IrH) occurs.[18] Comparing the new binuclear complexes, we observe (Table 1) that they display very similar values also similar to the value obtained for the parent mononuclear compounds. On the basis of this evidence, the IrH_2 moiety appears poorly sensitive to the vicinity of a second Group 8 transition metal and nearly unaffected by its formal oxidation state [compare (**8**) with (**9**)]. Unfortunately because of the lack of data concerning complex (**6**), we are not able to evaluate the effect exerted by the more acidic copper(II) centre.

On the other hand, for the azine species to act as an electronic channel between the two co-ordinated metals, a coplanar arrangement of the atoms involved in the $>C=N-N=C<$ bonds is required.[8] Therefore the resulting ineffectiveness displayed by these ligands may be due to the overall geometry of the complexes, wherein the two co-ordination planes are probably tilted around the N–N axis.

The reaction of all the heterobimetallic complexes (**6**)—(**9**), as well as the bis-dihydride (**4a**), with CO has been tested. These reactions were performed under mild conditions [*e.g.* room temperature and 1—3 atm (1 atm = 101 325 Pa) pressure] but the only reactivity detected was in the case of (**8**), wherein (**2a**) and $[PtMe_2(CO)_2]$ are formed (Experimental section). The platinum carbonyl species,[19] recognized by i.r. measurements carried out on the reaction mixture, is probably obtained by reaction of CO with an unidentified $PtMe_2$ compound resulting from the progressive dissociation of (**8**), according to the above mentioned equilibrium.

Experimental

General methods were as previously described.[10] In the n.m.r. data, unprimed symbols are reserved for the protons on the iridium-co-ordinated part of the azine ligands.

The ligands 2-pyridinecarbaldehyde azine (paa) and 6-methyl-2-pyridinecarbaldehyde azine (mpaa) were prepared by standard procedures.[20,21] Literature methods were used for the preparation of $[IrH_2(Me_2CO)_2(PPh_3)_2]X$ (X = PF_6 or SbF_6),[22] $[PdCl_2(PhCN)_2]$,[23] and $[PtMe_2(dmso)_2]$.[24]

Preparation of Compounds.—$[IrH_2(paa)(PPh_3)_2]PF_6$ (**2a**). A cold solution of $[IrH_2(Me_2CO)_2(PPh_3)_2]PF_6$ (**1a**) (0.200 g, 0.20 mmol) in CH_2Cl_2 (5 cm^3) was added to a stirred solution of paa (0.043 g, 0.20 mmol) in CH_2Cl_2 (3 cm^3) at 0 °C. The resulting orange solution was stirred at this temperature for 1 h and, after addition of diethyl ether (30 cm^3), refrigerated (−20 °C) overnight to give orange microcrystals of (**2a**) (0.210 g, 96%), m.p. 243—244 °C (Found: C, 52.3; H, 3.9; N, 4.7.

$C_{48}H_{42}F_6IrN_4P_3\cdot0.5\,CH_2Cl_2$ requires C, 52.2; H, 3.9; N, 5.0%). Molar conductivity: $\Lambda_m = 75.28\ \Omega^{-1}\ cm^2\ mol^{-1}\ (10^{-3}\ mol\ dm^{-3})$ in nitromethane. $\nu_{max.}$(IrH) 2 165br cm^{-1} (KBr). δ_H(300 MHz, CD_2Cl_2, standard $SiMe_4$) 6.83 [1 H, ddd, $J(H^5H^3) = 1.7$, $J(H^5H^4) = 7.4$, H^5 of py], 7.78—7.64 (3 H, m, H^4, $H^{4'}$, $H^{3'}$ of py), 8.15 [1 H, br d, $J(H^6H^5) = 5.5$, H^6 of py], 8.68 [1 H, ddd, $J(H^{6'}H^{5'}) = 4.8$, $J(H^{6'}H^{4'}) = 1.7$, $J(H^{6'}H^{3'}) = 1.0$ Hz, $H^{6'}$ of py], 8.83 (1 H, s, N=CH′), and 8.88 (1 H, br s, N=CH).

$[IrH_2(paa)(PPh_3)_2]SbF_6$ (**2b**). A yellow-orange crystalline product was obtained in a similar way from $[IrH_2(Me_2CO)_2(PPh_3)_2]SbF_6$ (**1b**) (0.300 g, 0.28 mmol) and paa (0.059 g, 0.28 mmol), yield 0.260 g (81%), m.p. 225—227 °C (Found: C, 48.0; H, 3.5; N, 4.5. $C_{48}H_{42}F_6IrN_4P_2Sb\cdot0.5\,CH_2Cl_2$ requires C, 48.2; H, 3.6; N, 4.6%). $\Lambda_m = 72.89\ \Omega^{-1}\ cm^2\ mol^{-1}\ (10^{-3}\ mol\ dm^{-3})$ in nitromethane. $\nu_{max.}$(IrH) 2 170br cm^{-1} (KBr); δ_H(300 MHz, CD_2Cl_2, standard $SiMe_4$) 6.83 [1 H, ddd, $J((H^4H^5) = 7.5$, $J(H^3H^5) = 1.6$, H^5 of py], 7.68 (1 H, br d, $H^{3'}$ of py), 7.74 [1 H, td, $J(H^{3'}H^{4'}) = 7.6$, $J(H^{4'}H^{6'}) = 1.8$, $H^{4'}$ of py], 7.75 [1 H, br t, $J(H^3H^4) = 7.8$, H^4 of py], 8.15 [1 H, br d, $J(H^5H^6) = 5.6$, H^6 of py], 8.68 [1 H, ddd, $J(H^{5'}H^{6'}) = 4.6$, $J(H^{3'}H^{6'}) = 1.2$, $H^{6'}$ of py], 8.83 (1 H, s, N=CH′), and 8.87 [1 H, d, $J = 1.2$ Hz, N=CH].

$[IrH_2(mpaa)(PPh_3)_2]PF_6$ (**3a**). A cold solution of complex (**1a**) (0.200 g, 0.20 mmol) in CH_2Cl_2 (5 cm^3) was added to a solution of mpaa (0.048 g, 0.20 mmol) in CH_2Cl_2 (3 cm^3) at 0 °C and the resulting yellow solution was stirred for 1 h. A yellow solid was obtained by slow addition of diethyl ether. Recrystallization from CH_2Cl_2–diethyl ether at −20 °C gave yellow needles of (**3a**) (0.180 g, 82%), m.p. 237 °C (Found: C, 53.4; H, 3.9; N, 4.8. $C_{50}H_{46}F_6IrN_4P_3\cdot0.5\,CH_2Cl_2$ requires C, 53.0; H, 4.1; N, 4.9%). $\Lambda_m = 78.30\ \Omega^{-1}\ cm^2\ mol^{-1}\ (10^{-3}\ mol\ dm^{-3})$ in nitromethane. $\nu_{max.}$(IrH) 2 240br and 2 150w cm^{-1} (KBr). δ_H(300 MHz, CD_2Cl_2, standard $SiMe_4$) 2.01 (3 H, s, CH_3), 2.63 (3 H, s, CH_3'), 6.89 [1 H, dd, $J(H^4H^5) = 8.0$, $J(H^3H^5) = 1.0$, H^5 of py], 7.46 (1 H, br d, H^3 of py), 7.49 (1 H, br d, $H^{3'}$ of py), 7.62 [1 H, t, $J(H^{3'}H^{4'}) = J(H^{4'}H^{5'}) = 8.0$, $H^{4'}$ of py], 7.65 [1 H, t, $J(H^3H^4) = 8.0$ Hz, H^4 of py], 8.84 (1 H, br s, N=CH), and 8.91 (1 H, s, N=CH′).

$[IrH_2(mpaa)(PPh_3)_2]SbF_6$ (**3b**). The analogous SbF_6^- salt was prepared in the same way, as orange needles, starting from (**1b**) (0.090 g, 0.084 mmol) and mpaa (0.020 g, 0.084 mmol), yield 0.093 g (95%), m.p. 260 °C (Found: C, 50.5, H, 4.2; N, 4.4. $C_{50}H_{46}F_6IrN_4P_2Sb$ requires C, 50.4; H, 3.9; N, 4.7%). $\Lambda_m = 79.80\ \Omega^{-1}\ cm^2\ mol^{-1}\ (10^{-3}\ mol\ dm^{-3})$ in nitromethane. $\nu_{max.}$(IrH) 2 300 and 2 160 cm^{-1} (KBr). δ_H(300 MHz, CD_2Cl_2, standard $SiMe_4$) 2.00 (3 H, s, CH_3), 2.63 (3 H, s, CH'_3), 6.89 [1 H, dd, $J(H^4H^5) = 8.0$, $J(H^3H^5) = 1.2$, H^5 of py], 7.48 (1 H, dd, H^3 of py), 7.50 (1 H, br d, $H^{3'}$ of py), 7.63 [1 H, t, $J(H^{3'}H^{4'}) = 7.4$ Hz, $H^{4'}$ of py], 7.65 [1 H, t, $J(H^3H^4) = 7.9$, H^4 of py], 8.83 (1 H, br s, N=CH), and 8.92 (1 H, s, N=CH′).

$[\{IrH_2(PPh_3)_2\}_2(\mu\text{-}paa)][PF_6]_2$ (**4a**). A solution of complex (**1a**) (0.090 g, 0.093 mmol) in CH_2Cl_2 (5 cm^3) was added to a solution of (**2a**) (0.100 g, 0.093 mmol) in CH_2Cl_2 (10 cm^3) and the resulting deep red solution stirred at room temperature for 1 h. A red microcrystalline precipitate of (**4a**) was obtained by diffusion of n-hexane (10 cm^3) through the solution at −20 °C (0.160 g, 86%), m.p. 255—256 °C (Found: C, 51.5; H, 3.6; N, 2.9. $C_{84}H_{74}F_{12}Ir_2N_4P_6$ requires C, 52.0; H, 3.8; N, 2.9%). $\Lambda_m = 163.26\ \Omega^{-1}\ cm^2\ mol^{-1}\ (10^{-3}\ mol\ dm^{-3})$ in nitromethane. $\nu_{max.}$(IrH) 2 120 and 2 110 cm^{-1}. δ_H(300 MHz, CD_2Cl_2, standard $SiMe_4$) 6.52 [2 H, ddd, $J(H^5H^6) = 5.5$, $J(H^4H^5) = 7.7$, $J(H^3H^5) = 1.3$, H^5 of py], 8.11 [2 H, t, $J(H^3H^4) = 7.5$ Hz, H^4 of py], 8.47 (2 H, br d, H^3 of py), and 10.4 (2 H, br s, N=CH).

$[\{IrH_2(PPh_3)_2\}_2(\mu\text{-}paa)][SbF_6]_2$ (**4b**). From complexes (**2b**) (0.100 g, 0.086 mmol) and (**1b**) (0.092 g, 0.086 mmol) were obtained in the same manner dark red microcrystals of (**4b**)(0.165 g, 89%), m.p. 267 °C (Found: C, 47.7; H, 3.4; N, 2.7. $C_{84}H_{74}F_{12}Ir_2N_4P_4Sb_2$ requires C, 47.6; H, 3.5; N, 2.6%). $\Lambda_m = 165.88\ \Omega^{-1}\ cm^2\ mol^{-1}\ (10^{-3}\ mol\ dm^{-3})$ in nitromethane. $\nu_{max.}$(IrH) 2 280 and 2 120 cm^{-1} (KBr). δ_H(300 MHz, CD_2Cl_2, standard $SiMe_4$) 6.52 (2 H, m, H^5 of py), 8.08 [2 H, t, $J(H^4H^5) = 7.6$, H^4 of py], 8.43 [2 H, d, $J(H^3H^4) = 7.9$ Hz, H^3 of py], and 10.45 (2 H, s, N=CH).

$[\{IrH_2(PPh_3)_2\}_2(\mu\text{-}mpaa)][PF_6]_2$ (**5a**). To a solution of complex (**3a**) (0.100 g, 0.091 mmol) in CH_2Cl_2 (5 cm^3) was added a solution of (**1a**) (0.090 g, 0.091 mmol) in CH_2Cl_2 (5 cm^3) and the resulting deep red solution stirred for 2 h. A cherry red solid was formed upon slow addition of diethyl ether and was crystallized from CH_2Cl_2–EtOH (0.166 g, 92%), m.p. 254 °C (Found: C, 51.4; H, 4.0; N, 2.7. $C_{86}H_{78}F_{12}Ir_2N_4P_6\cdot CH_2Cl_2$ requires C, 51.0; H, 3.9; N, 2.7%). $\Lambda_m = 163.08\ \Omega^{-1}\ cm^2\ mol^{-1}\ (10^{-3}\ mol\ dm^{-3})$ in nitromethane. $\nu_{max.}$(IrH) 2 310 and 2 160 cm^{-1} (KBr). δ_H(300 MHz, CD_2Cl_2, standard $SiMe_4$) 1.64 (6 H, s, CH_3), 6.90 [2 H, dd, $J(H^4H^5) = 7.8$, $J(H^3H^5) = 1.0$, H^5 of py], 8.16 [2 H, t, $J(H^3H^4) = 8.0$ Hz, H^4 of py], 8.50 (2 H, br d, H^3 of py), and 10.50 (2 H, br s, N=CH).

$[\{IrH_2(PPh_3)_2\}_2(\mu\text{-}mpaa)][SbF_6]_2$ (**5b**). From the reaction of complex (**3b**) (0.060 g, 0.05 mmol) and (**1b**) (0.054 g, 0.05 mmol), carried out as above, a dark red solid was obtained which was crystallized from CH_2Cl_2–EtOH (0.100 g, 95%), m.p. 288 °C (Found: C, 48.1; H, 3.6; N, 2.7. $C_{86}H_{78}F_{12}Ir_2N_4P_4Sb_2$ requires C, 48.1; H, 3.7; N, 2.6%). $\Lambda_m = 171.60\ \Omega^{-1}\ cm^2\ mol^{-1}\ (10^{-3}\ mol\ dm^{-3})$ in nitromethane. $\nu_{max.}$(IrH) 2 310 and 2 150br cm^{-1} (KBr). δ_H (300 MHz, CD_2Cl_2, standard $SiMe_4$) 6.90 [2 H, d, $J(H^4H^5) = 7.8$, H^5 of py], 8.13 (2 H, t, H^4 of py), 8.47 [2 H, br d, $J(H^3H^4) = 7.0$ Hz, H^3 of py], and 10.51 (2 H, s, N=CH).

$[(Ph_3P)_2H_2Ir(\mu\text{-}paa)CuCl_2]PF_6$ (**6**). To a solution of complex (**2a**) (0.100 g, 0.093 mmol) in CH_2Cl_2 (5 cm^3) was added a solution of $CuCl_2\cdot2H_2O$ (0.016 g, 0.093 mmol) in ethanol (10 cm^3). The solution rapidly turned orange-red. After 1 h it was concentrated under vacuum and the orange solid formed was filtered off, washed with diethyl ether, and vacuum dried (0.094 g, 84%), m.p. 174—175 °C (Found: C, 46.9; H, 3.5; N, 4.6. $C_{48}H_{42}Cl_2CuF_6IrN_4P_3$ requires C, 47.7; H, 3.5; N, 4.6%). $\Lambda_m = 78.90\ \Omega^{-1}\ cm^2\ mol^{-1}\ (10^{-3}\ mol\ dm^{-3})$ in nitromethane. $\nu_{max.}$(IrH) 2 180br (KBr); $\nu_{max.}$(CuCl) 350—320 cm^{-1} (CsI).

$[(Ph_3P)_2H_2Ir(\mu\text{-}paa)PdCl_2]PF_6$ (**7**). A solution of $[PdCl_2(PhCN)_2]$ (0.029 g, 0.075 mmol) in CH_2Cl_2 (3 cm^3) was added to a stirred solution of (**2a**) (0.080 g, 0.075 mmol) in CH_2Cl_2 (2 cm^3). The solution immediately turned red and was left for 30 min. Addition of diethyl ether (15 cm^3) resulted in the precipitation of (**7**), which was recrystallized from CH_2Cl_2–Et_2O at −20 °C as red plates (0.082 g, 88%), m.p. 202—203 °C (Found: C, 45.3; H, 3.2; N, 4.3. $C_{48}H_{42}Cl_2F_6IrN_4P_3Pd\cdot0.5\,CH_2Cl_2$ requires C, 45.0; H, 3.3; N, 4.3%). $\Lambda_m = 77.00\ \Omega^{-1}\ cm^2\ mol^{-1}\ (10^{-3}\ mol\ dm^{-3})$ in nitromethane. $\nu_{max.}$(IrH) 2 185br (KBr); $\nu_{max.}$(PdCl) 375—360 cm^{-1} (CsI). δ_H(300 MHz, CD_2Cl_2, standard $SiMe_4$) 6.79 (1 H, m, H^5 of py), 7.64 [1 H, ddd, $J(H^{4'}H^{5'}) = 7.8$, $J(H^{3'}H^{5'}) = 1.2$, $H^{5'}$ of py], 7.72 (2 H, d, H^4 and H^3 of py), 8.09 [1 H, br d, $J(H^5H^6) = 5.2$, H^6 of py], 8.22 (1 H, s, N=CH′), 8.23 [1 H, t, $J(H^{3'}H^{4'}) = 7.8$, $H^{4'}$ of py], 8.75 [1 H, dd, $J(H^{5'}H^{6'}) = 5.3$, $J(H^{4'}H^{6'}) = 1.2$ Hz, $H^{6'}$ of py], and 9.79 (1 H, br s, N=CH).

$[(Ph_3P)_2H_2Ir(\mu\text{-}paa)PtMe_2]PF_6$ (**8**). To a solution of complex (**2a**) (0.100 g, 0.093 mmol) in acetone (3 cm^3) was added a solution of $[PtMe_2(dmso)_2]$ (0.036 g, 0.093 mmol) in dry benzene (5 cm^3). The reaction mixture was left to stand for 2 h after which time a dark green solution had developed. The solvent was removed under reduced pressure and the residue was triturated with diethyl ether to give (**8**) as a green solid (0.110 g, 91%), m.p. 198 °C (decomp.) (Found: C, 47.7; H, 3.7; N, 4.3. $C_{50}H_{48}F_6IrN_4P_3Pt$ requires C, 46.2; H, 3.7; N, 4.3%). $\Lambda_m = 78.50\ \Omega^{-1}\ cm^2\ mol^{-1}\ (10^{-3}\ mol\ dm^{-3})$ in nitromethane. $\nu_{max.}$(IrH) 2 260—2 180 cm^{-1} (KBr). δ_H(300 MHz, CD_2Cl_2, standard $SiMe_4$) 0.76 [3 H, s, $^2J(PtH) = 85.0$, CH_3–Pt], 1.23 [3 H, s, $^2J(PtH) = 90.0$, CH_3–Pt], 6.84 [1 H, ddd, $J(H^4H^5) = 7.5$, $J(H^3H^5) = 1.2$, H^5 of py], 7.60 [1 H, br d, $J(H^{5'}H^{6'}) = 5.5$,

Table 3. Fractional co-ordinates (× 10^4) with estimated standard deviations in parentheses for the non-hydrogen atoms*

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ir(1)	8 351(1)	2 388(1)	1 774(1)	C(19)	10 650(9)	1 619(7)	5 619(9)
Sb(1)	4 563(1)	3 184(1)	6 886(1)	C(20)	9 915(8)	1 686(6)	4 503(9)
P(1)	7 918(2)	1 228(2)	2 553(2)	C(21)	7 734(7)	93(6)	1 726(8)
P(2)	9 183(2)	3 482(2)	1 203(2)	C(22)	7 066(8)	−631(7)	1 800(9)
N(1)	7 254(7)	3 104(5)	2 144(7)	C(23)	7 026(9)	−1 486(8)	1 252(10)
N(2)	6 928(6)	1 981(5)	138(7)	C(24)	7 614(10)	−1 639(9)	598(11)
N(3)	6 659(7)	1 411(5)	−1 020(7)	C(25)	8 267(10)	−950(8)	508(11)
N(4)	7 846(7)	−132((5)	−2 080(7)	C(26)	8 335(9)	−65(7)	1 089(9)
C(1)	7 435(10)	3 716(7)	3 156(11)	C(27)	6 677(8)	1 238(6)	2 695(9)
C(2)	6 600(13)	4 104(9)	3 218(14)	C(28)	6 668(9)	1 713(7)	3 718(10)
C(3)	5 631(13)	3 887(10)	2 279(16)	C(29)	5 698(11)	1 836(9)	3 760(12)
C(4)	5 458(11)	3 279(8)	1 261(14)	C(30)	4 756(11)	1 452(9)	2 719(12)
C(5)	6 259(8)	2 911(7)	1 218(10)	C(31)	4 742(11)	1 005(8)	1 731(12)
C(6)	6 137(8)	2 288(6)	157(9)	C(32)	5 728(9)	890(7)	1 692(10)
C(7)	7 385(9)	1 045(6)	−1 087(9)	C(33)	10 628(8)	3 837(6)	2 031(8)
C(8)	7 216(8)	459(7)	−2 227(9)	C(34)	11 150(10)	3 723(8)	3 152(11)
C(9)	6 516(9)	533(8)	−3 297(10)	C(35)	12 264(10)	4 016(8)	3 780(12)
C(10)	6 429(11)	−48(9)	−4 318(10)	C(36)	12 825(11)	4 383(8)	3 228(12)
C(11)	7 000(10)	−698(8)	−4 210(11)	C(37)	12 326(11)	4 512(9)	2 098(12)
C(12)	7 683(10)	−731(7)	−3 084(13)	C(38)	11 208(10)	4 229(8)	1 487(11)
C(13)	8 489(11)	3 930(9)	4 167(10)	C(39)	9 032(7)	3 132(6)	−336(8)
C(14)	8 340(13)	−1 402(10)	−2 879(15)	C(40)	8 372(8)	3 427(7)	−1 301(9)
F(1)	4 721(10)	4 285(8)	6 649(11)	C(41)	8 242(10)	3 061(8)	−2 458(11)
F(2)	4 583(11)	3 536(10)	8 402(13)	C(42)	8 762(10)	2 417(8)	−2 660(12)
F(3)	4 394(11)	2 033(9)	7 084(12)	C(43)	9 422(9)	2 126(8)	−1 723(10)
F(4)	4 468(10)	2 792(8)	5 408(11)	C(44)	9 547(9)	2 475(7)	−567(10)
F(5)	3 119(10)	2 991(8)	6 151(11)	C(45)	8 699(8)	4 511(7)	1 306(9)
F(6)	5 940(14)	3 293(11)	7 633(16)	C(46)	7 662(9)	4 489(8)	678(10)
C(15)	8 876(7)	1 199(6)	4 043(8)	C(47)	7 252(11)	5 252(9)	858(12)
C(16)	8 587(8)	647(6)	4 671(9)	C(48)	7 900(11)	5 980(10)	1 681(12)
C(17)	9 334(8)	587(7)	5 766(9)	C(49)	8 926(13)	6 024(11)	2 312(14)
C(18)	10 342(8)	1 059(7)	6 217(9)	C(50)	9 387(11)	5 294(8)	2 133(11)

* The co-ordinates of the two hydrides are: H′ 9 137, 1 923, 1 753; H″ 9 107, 2 621, 2 916.

^3J(PtH) = 22.0, $H^{6'}$ of py], 7.77—7.66 (2 H, m, H^4 and $H^{5'}$ of py), 8.06 [1 H, br d, $J(H^5H^6)$ = 5.4, H^6 of py], 8.16 [1 H, td, $J(H^{4'}H^{5'}) = J(H^{3'}H^{4'})$ = 7.8, $J(H^{4'}H^{6'})$ = 1.3, $H^{4'}$ of py], 9.36 (1 H, br s, N=CH), and 9.75 [1 H, s, ^3J(PtH) = 17.4 Hz, N=CH′].

[$(Ph_3P)_2H_2Ir(\mu$-paa)$PtMe_3(I)]PF_6$ (**9**). To a solution of complex (**8**) (0.050 g, 0.038 mmol) in acetone (10 cm^3) was added an excess of MeI (0.03 cm^3). The solution immediately turned red-orange. The solvent was removed under reduced pressure and the oily residue redissolved in CH_2Cl_2 (5 cm^3). Pentane (15 cm^3) was added to this solution giving an orange precipitate of (**9**) (0.045 g, 81%), m.p. 183—185 °C (Found: C, 42.2; H, 3.6; N, 3.7. $C_{51}H_{51}F_6IIrN_4P_3Pt$ requires C, 42.5; H, 3.6; N, 3.9%). Λ_m = 81.50 Ω^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3}) in nitromethane. $\nu_{max.}$(IrH) 2 180br cm^{-1} (KBr). δ_H(300 MHz, CD_2Cl_2, standard $SiMe_4$) −0.32 [3 H, s, ^2J(PtH) = 69.0, CH_3–Pt *trans* to the iodide group], 1.36 [3 H, s, ^2J(PtH) = 71.2, CH_3-Pt], 1.63 [3 H, s, ^2J(PtH) = 75.0, CH_3-Pt], 6.97 [1 H, ddd, $J(H^4H^5)$ = 7.8, $J(H^3H^5)$ = 1.3, H^5 of py], 7.61 [1 H, td, $J(H^3H^4)$ = 8.0, $J(H^4H^6)$ = 1.3, H^4 of py], 7.77 [1 H, ddd, $J(H^{3'}H^{5'})$ = 1.2, $H^{5'}$ of py], 8.15 [1 H, td, $J(H^{4'}H^{5'}) = J(H^{3'}H^{4'})$ = 7.9, $J(H^{4'}H^{6'})$ = 1.3, $H^{4'}$ of py], 8.53 [1 H, br d, $J(H^5H^6)$ = 5.3, H^6 of py], 8.86 [1 H, br d, $J(H^{5'}H^{6'})$ = 6.0, ^3J(PtH) = 13.0, $H^{6'}$ of py], 9.43 [1 H, s, ^3J(PtH) = 15.5 Hz, N=CH′], and 9.70 (1 H, br s, N=CH).

Reaction of [$(Ph_3P)_2H_2Ir(\mu$-paa)$PtMe_2]PF_6$ (**8**) *with* CO.—Carbon monoxide was bubbled through a green solution of complex (**8**) in CH_2Cl_2. Over 5 min the solution turned orange. An i.r. spectrum of the solution showed two ν(CO) bands at 2 115 and 2 065 cm^{-1}, consistent with the presence of [$PtMe_2(CO)_2$].[19] The solvent was then removed under vacuum. Infrared and n.m.r. data of the resulting solid were identical to those of a pure sample of [$IrH_2(paa)(PPh_3)_2]PF_6$ (**2a**).

Crystal Structure Determination of Complex (**3b**).—*Crystal data.* $C_{50}H_{46}F_6IrN_4P_2Sb$, M = 1 192.8, triclinic, space group $P\bar{1}$, a = 14.017(6), b = 15.673(7), c = 12.452(6) Å, α = 99.60(1), β = 112.78(2), γ = 97.88(2)°, U = 2 425(2) Å^3 (by least-squares refinement of the 2θ values of 30 accurately measured reflections), Z = 2, λ = 0.710 69 Å, D_c = 1.63 g cm^{-3}, $F(000)$ = 1 172, μ(Mo-K_α) = 34.1 cm^{-1}.

A crystal of approximate dimensions 0.25 × 0.30 × 0.35 mm was used for the structure analysis. A correction for absorption[25] was applied (maximum and minimum transmission factors were 1.150 and 0.879) using the program ABSORB.[26]

Data collection and processing. Siemens AED diffractometer, θ—2θ scan mode, using niobium-filtered Mo-K_α radiation; all the reflections with θ in the range 3—25° were measured. Of 8 202 independent reflections, 5 675, having $I > 2\sigma(I)$, were considered observed and used in the analysis.

Structure solution and refinement. Patterson and Fourier methods, full-matrix least squares with anisotropic thermal parameters in the last cycles for all the non-hydrogen atoms except the fluorine and the carbon atoms of the phenyl rings. All the hydrogen atoms, except the hydrides [clearly located in the final Fourier difference map even if at distances from the Ir atom shorter than expected (Ir–H′ 1.41 and Ir–H″ 1.35 Å)] were placed at their geometrically calculated positions and introduced in the final structure-factor calculation. The weighting scheme used in the last cycles of refinement was $w = K[\sigma^2(F_o + gF_o]^{-1}$ with K = 0.6096 and g = 0.0023. Final R

and R' values were 0.049 and 0.060 respectively. The SHELX system of computer programs was used.[27] Atomic scattering factors, corrected for anomalous dispersion of Ir, Sb, and P, were taken from ref. 28. All calculations were performed on the CRAY X-MP/12 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna. Final atomic co-ordinates for the non-hydrogen atoms are given in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

Acknowledgements

We thank the Italian Ministero della Pubblica Istruzione for financial support.

References

1 R. M. Bullock and C. P. Casey, *Acc. Chem. Res.*, 1987, **20**, 167.
2 R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc.*, 1976, **98**, 2134.
3 M. Ghedini, F. Neve, A. M. Manotti Lanfredi, and F. Ugozzoli, *Inorg. Chim. Acta*, 1988, **147**, 243.
4 A. M. Manotti Lanfredi, A. Tiripicchio, F. Ugozzoli, M. Ghedini, and F. Neve, *J. Chem. Soc., Dalton Trans.*, 1988, 651.
5 B. D. Alexander, B. J. Johnson, S. M. Johnson, A. L. Casalnuovo, and L. H. Pignolet, *J. Am. Chem. Soc.*, 1986, **108**, 4409.
6 J. R. Shapley, R. R. Schrock, and J. A. Osborn, *J. Am. Chem. Soc.*, 1969, **91**, 2816.
7 A. Dei, D. Gatteschi, and E. Piergentili, *Inorg. Chem.*, 1979, **18**, 89.
8 C. J. O'Connor, R. J. Romananch, D. M. Robertson, E. E. Edouk, and F. R. Fronczek, *Inorg. Chem.*, 1983, **22**, 449.
9 T. C. Woon, L. K. Thompson, and P. Robichaud, *Inorg. Chim. Acta*, 1984, **90**, 201.
10 M. Ghedini, M. Longeri, and F. Neve, *J. Chem. Soc., Dalton Trans.*, 1986, 2669.
11 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
12 M. Laurin, E. N. Holt, and R. H. Crabtree, *Organometallics*, 1989, **8**, 99.
13 A. C. Hazell, Abstracts, 18th Danish Crystallography Meeting, Risø, Denmark, Wiley, New York, 1982, paper 24.
14 G. Nord, A. C. Hazell, R. G. Hazell, and O. Farver, *Inorg. Chem.*, 1983, **22**, 3429.
15 J. R. Ferraro, 'Low-Frequency Vibrations of Inorganic and Coordination Compounds,' Plenum, New York, 1971.
16 J. D. Scott and R. J. Puddephatt, *Organometallics*, 1986, **5**, 2522.
17 P. K. Monaghan and R. J. Puddephatt, *Organometallics*, 1985, **4**, 1406.
18 B. Olgemöller and W. Beck, *Inorg. Chem.*, 1983, **22**, 997.
19 G. K. Anderson, H. C. Clark, and J. A. Davis, *Inorg. Chem.*, 1981, **20**, 1636.
20 W. J. Stratton and D. H. Busch, *J. Am. Chem. Soc.*, 1958, **80**, 1286.
21 W. Baker, K. M. Buggle, J. F. W. McOmie, and D. A. M. Watkins, *J. Chem. Soc.*, 1958, 3594.
22 R. H. Crabtree, M. F. Mellea, J. M. Mihelcic, and J. M. Quirk, *J. Am. Chem., Soc.*, 1982, **104**, 107.
23 M. S. Karasch, R. C. Seyler, and F. R. Mayo, *J. Am. Chem. Soc.*, 1938, **60**, 882.
24 C. Eaborn, K. Kundu, and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1981, 933.
25 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
26 F. Ugozzoli, *Comput. Chem.*, 1987, **11**, 109.
27 G. M. Sheldrick, SHELX Program for crystal structure determination, University of Cambridge, 1976.
28 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

Received 9th May 1988; *Paper* 8/01809J